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Kinetics of the Gas-Phase Thermal Chlorination of Methane

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Abstract—Based on information concerning the rate constants of elementary steps corrected with consideration for experimental data obtained under laboratory, pilot-plant, and industrial conditions, the kinetics of the gas-phase process of thermal chlorination of methane was considered. The form of the rate equation of the process depends on the mode of chain termination. Of four possible variants, cross termination with the participation of a chlorine atom and a hydrocarbon radical and quadratic-law termination on hydrocarbon radicals are significant under industrial conditions. The fractions of the participation of either of these variants at various degrees of chlorine conversion were determined. Rate equations were found to describe the chlorination of methane, methyl chloride, methylene chloride, and chloroform with cross and quadratic-law chain terminations. The overall kinetic order of these equations with respect to reactants was 1.5. Combined equations that imply the simultaneous occurrence of cross and quadratic-law chain terminations were proposed.

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INTRODUCTION

The gas-phase thermal chlorination of methane has long been widely used in industry; however, only a small number of publications devoted to the kinetics of this process are known. In an early study, Pease and Walz [1] found that the rate of chlorine consumption was proportional to the partial pressures of chlorine and methane; that is, the overall reaction was of second order and the activation energy was 132.3 kJ/mol. Under the same conditions, the rate of chlorination of methyl chloride was higher than that of methane by a factor of about 2, whereas, on the contrary, the rates of chlorination of methylene chloride and chloroform were lower than that of methane.

Much more recently, Aglulin et al. [2] also found kinetic orders close to unity with respect to methane and chlorine in the thermal reaction of methane chlorination. The apparent activation energy was 121.3 ± 8.4 kJ/mol. According to Aglulin et al. [2], the rate of methane chlorination under comparable conditions was higher by a factor of about 2 than that found earlier by Arai et al. [3]. In our opinion, this discrepancy can be due to the fact that Aglulin et al. [2] performed the study in a flow-circulation setup with a considerable portion of the circulation loop in the light, which could facilitate an additional photochemical initiation of the chlorination reaction.

Arai et al. [3] performed the most comprehensive study of the kinetics of gas-phase thermal chlorination of not only methane but also its chlorinated derivatives. They proposed a rate equation for the process, in which orders with respect to chlorine and methane (or corresponding chloromethanes) were equal to unity.

However, a comparison between the results of calculations performed with the use of the kinetic model by Arai et al. [3] and the data obtained in operating industrial reactors, pilot plants, and laboratory setups revealed considerable differences. This inconsistence stimulated us to consider this problem in more detail.

EXPERIMENTAL

A hollow lined reactor with a brick column arranged at the center is used in industry for chlorination (this technology was developed in prewar Germany). The initial cold mixture, impinging on the central column, is heated partially from the reaction walls, partially as a result of mixing with a hot reaction gas, and partially by thermal emission from the brickwork. The process is performed at 480–500°C.

The regime of gas motion in these reactors, which were removed from Germany as reparations after the war, is unknown, and it cannot be described by either a plug-flow model or a well-mixed model. It is likely that this regime is close to the latter case. Therefore, to evaluate the ratio between the rate constants of chlorination of methane and methyl chloride in an industrial reactor, we used only data on the steady-state concentration of methyl chloride in the reaction gas (under conditions of a recycle process with the complete return of methyl chloride to the chlorinator). Industrial reactors operate at an excess pressure of no higher than 0.7 atm (usually, 0.5–0.6 atm) and a temperature of 480–500°C.

At many plants for the manufacture of chloromethanes, in particular, in Russia, the recycle of methyl chloride is used and only methylene chloride

Table 1. Composition of the chloromethanes obtained upon methane chlorination

Temperature, °C	Composition of chloromethanes, wt %			
	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Laboratory data obtained in this work ($CH_4 : Cl_2 = 5$)				
380	82.00	15.95	2.00	0.05
420	74.10	21.06	4.58	0.26
460	68.06	24.50	6.88	0.56
500	66.32	25.21	7.58	0.89
Calculation from published data [3] ($CH_4 : Cl_2 = 1$)				
380	52.70	36.85	9.86	0.59
420	61.35	32.51	5.85	0.29
460	68.44	27.87	3.55	0.14
500	74.08	23.66	2.19	0.07

and chloroform are separated as commercial products. Methyl chloride is returned to the reactor simultaneously with the return of excess methane, which is required for explosion-proof operation and heat removal from the reaction occurring in a hollow adiabatic reactor. The conversion of methane is about 15%, and the conversion of chlorine is 99.9% or higher.

The pilot reactor with internal recycle is a mixing apparatus 800 mm in diameter and 3 m in cylindrical part height [4]. A cold starting mixture is introduced into the reactor at a high rate through a nozzle. Because of this, conditions for the injection of two to four volumes of hot reaction gas are generated. After mixing in a tube arranged at the center of the reactor, the temperature of the mixed flow reaches the temperature of the onset of reaction and almost the entire chlorination process occurs in the ring space between the central tube and reactor walls. Chlorine does almost not participate in the internal recycle because it almost completely reacts in the ring space.

We used data obtained in the pilot reactor to evaluate the accuracy of calculation results at high degrees of chlorine conversion (x_{Cl}) and to estimate the effect of pressure on x_{Cl}. The reaction was performed in the pilot reactor at an excess pressure of no higher than 1.5 atm. Circulation gas from an operating facility or, sometimes, methane was mainly supplied for chlorination. The temperature was maintained within a range of 400–420°C. These parameters, as well as the rate of supply and the composition of starting reactants, in the pilot and industrial plants differed only slightly, if any.

The main kinetic data on the effects of temperature, contact time, and initial reactant concentrations on the rate of reaction were obtained in laboratory reactors. The reactor pressure was somewhat higher than atmospheric pressure because of the resistance produced by Drexel bottles filled with a solution of potassium iodide to absorb chlorine and hydrogen chloride (~100 mm of water).

The laboratory experiments on methane chlorination in a hollow volume were performed in two types of reactors. A reactor close to the model of a plug-flow apparatus was 20 mm in diameter and 150 mm in length; a thermocouple 7 mm in diameter was arranged within the reactor. A reactor close to the model of a well-mixed apparatus was 80 mm in diameter and 50 mm in height; a stirrer was placed within it. The reactors were heated with an external electric heating unit.

The ethane content of methane was no higher than 0.01 vol %, and the methane purity was no less than 99.88%. The impurity of oxygen in chlorine was no higher than 0.005%, and the purity of chlorine was no less than 99.7%.

The gas chromatographic analyses of the reaction mixture in laboratory, pilot, and industrial setups were performed after washing the reaction mixture in Drexel bottles filled with a solution of potassium iodide to remove chlorine and hydrogen chloride and drying with calcium chloride. Triphenyl phosphate on Sferokhrom was used as a stationary phase; the column length was 6 m, and the column temperature was 100°C. The contents of Drexel bottles were titrated with a solution of sodium thiosulfate to determine the amount of unreacted chlorine and then with an alkali solution to determine the amount of released hydrogen chloride.

RESULTS AND DISCUSSION

The reliability of experimental and calculated data was checked using several tests. First, this is the rate of the process on which the reactor volume required for reaching a specified value of x_{Cl} depends. The rate of reaction calculated from published data [3] was found overestimated, especially, in experiments performed at a pilot plant under pressure. This can be due to the fact that the overall order of reaction with respect to starting reactants, which was taken by Arai et al. [3], is 2, whereas the overall order of reaction is 1.5 in three other alternative kinetic schemes (see below).

Another difference of data published by Arai et al. [3] from our experimental results is a higher (by a factor of ~2) yield of methyl chloride and lower (also by a factor of ~2) yields of chloroform and carbon tetrachloride. Moreover, according to activation energies found by Arai et al. [3], the yields of chloroform and CCl_4 would increase with temperature, whereas they monotonically increased in accordance with our laboratory data (Table 1).

The calculation performed under the same conditions (the molar ratio $CH_4 : Cl_2 = 5$) based on kinetic data [3] afforded the yield of CCl_4 lower than 0.01% even at 350°C. For clarity, we calculated x_{Cl} at $CH_4 : Cl_2 = 1$, when the yields of chloroform and CCl_4 became considerable (Table 1). We did not perform

experiments at this ratio in a hollow reactor because an explosive mixture is formed in this case.

Another adequacy test for the kinetic model of the methane chlorination process is the concentration of methyl chloride in the reaction gas under recycling conditions. The concentrations of methyl chloride in circulation and reaction gases varied from 10 to 17 mol % depending on CH_3Cl losses. At the same time, the calculation of the process with methyl chloride recycling based on kinetic data [3] gives 42% at a temperature of 350°C; this value suggests the inadequacy of the kinetic scheme [3].

Finally, the last test, which seems theoretically important but is actually of great practical use, is the character of chain termination. The fact of the matter is that chlorinated C_2 hydrocarbon impurities, which make the target products (commercial chloromethanes) difficult to separate, are formed upon quadratic-law termination.

The boiling temperatures of such impurities are close to the boiling temperature of a chlorinated methane derivative (for example, cf. T_b of 1,1-dichloroethane and *cis*-1,2-dichloroethylene with T_b of chloroform); other impurities form azeotropic mixtures boiling close to the main component (1,2-dichloroethane with CCl_4 or, according to our data, 1,1-dichloroethane with chloroform). In this case, it should be borne in mind that requirements imposed on the concentrations of individual impurities are rigid: the concentrations of 1,1-dichloroethane in chloroform and 1,2-dichloroethane in carbon tetrachloride should be no higher than 0.002%. To remove the above impurities from chloromethanes, the process is usually performed in a batch mode; this results in product losses, additional consumption of materials and other resources, and the formation of a large amount of wastes. For the purification of methylene chloride, it was proposed to treat it with a solution of potassium permanganate. In industry, pure and dry chloroform (separated by rectification) containing only 0.03% 1,1-dichloroethane is stirred with oleum for 6 h; then, it is neutralized with a solution of sodium hydroxide and subjected to azeotropic drying on a rectification column with 100 plates.

However, this subject matter should be considered individually; here, we will select an area directly concerning the subject matter of this work. Preliminary results suggested that it is desirable to exclude quadratic-law chain termination on hydrocarbon radicals.

The reaction mechanism of chain termination on a wall corresponds to the first orders of reaction with respect to chlorine and methane. The use of a relatively long (60 cm) and narrow (2 cm in diameter) reactor by Arai et al. [3] and a low process temperature (275–370°C), at which chain initiation could mainly occur on a wall [5], could be favorable for this mechanism.

Having data on the reaction kinetics of elementary steps in the radical chain chlorination of methane and using the method of steady-state concentrations, we can calculate the kinetics of the overall process [6]:

Chain initiation

(1) $Cl_2 \xrightarrow{k_1} Cl^{\cdot} + Cl^{\cdot}$.

Chain propagation

(2) $Cl^{\cdot} + RH \xrightarrow{k_2} HCl + R^{\cdot}$;

(3) $R^{\cdot} + Cl_2 \xrightarrow{k_3} RCl + Cl^{\cdot}$.

Chain termination

(4) $Cl^{\cdot} + Cl^{\cdot} + M \xrightarrow{k_4} Cl_2 + M$,

(5) $R^{\cdot} + R^{\cdot} \xrightarrow{k_5} R-R$,

(6) $R^{\cdot} + Cl^{\cdot} \xrightarrow{k_6} RCl$,

(7) $Cl^{\cdot} + wall \xrightarrow{k_7} Cl_{ads}$.

Different rate equations can correspond to the reaction scheme depending on the predominance of a particular termination reaction. The orders of these reactions with respect to chlorine or methane varied from 0.5 to 1.5 or from 0 to 1, respectively [6]:

$$w_4 = k_2\sqrt{k_1/k_4}\,p_{CH4}\,p_{Cl_2}^{0.5},$$

$$w_5 = k_3\sqrt{k_1/k_5}\,p_{Cl_2}^{1.5},$$

$$w_6 = \sqrt{k_1k_2k_3/k_6}\,p_{CH_4}^{0.5}p_{Cl_2},$$

$$w_7 = (k_1k_2/k_7)p_{CH_4}p_{Cl_2},$$

were k_1–k_7 are the rate constants of corresponding steps 1–7, and p_{CH_4} and p_{Cl_2} are the partial pressures of methane and chlorine, respectively.

The direct recombination of chlorine radicals is improbable because the recombination energy is sufficient for the decomposition of the resulting chlorine molecule into atoms. The probability of the reaction of quadratic-law chain termination on chlorine radicals with energy transfer to inert particle M is also low because it implies the simultaneous collision of three particles.

According to Emanuel' and Knorre [7], the concentration of chlorine atoms should be higher than the concentration of hydrocarbon radicals $R^{\cdot}$ by a factor of about 10^4 in order that the rate of recombination on chlorine radicals with inert particle M may be commensurable with the rate of cross termination or termination on hydrocarbon radicals. At elevated pressures, a certain contribution from quadratic-law termination on chlorine radicals should be taken into account because of an increase in the rate of trimolecular reaction of chlorine radicals with particle M.

The reactions of cross termination and quadratic-law termination on hydrocarbon radicals can occur because the energy released in this case is distributed over many bonds to protect the resulting molecule from decomposition for a time. Within this time interval, this molecule manages to collide with another molecule and to transfer a portion of its excess energy to it. It was reliably established that the recombination reaction of methyl radicals $2\dot{C}H_3 \rightarrow C_2H_6$ occurs at each binary collision [8].

Thus, there are two other ways for excluding or decreasing the formation of chlorinated C_2 hydrocarbon impurities: first, to exclude quadratic-law termination on hydrocarbon radicals by generating conditions for termination on the wall and, second, to increase the chain length.

Decreasing temperature in order to increase the chain length, we managed to decrease the formation of impurities; however, this decrease was insufficient [9]; in addition, the rate of the main process decreased at a lower temperature.

The chlorination of methane in a flow reactor without and with filling the reactor volume with glass rings for increasing the wall surface area [10] did not change both quantitative and qualitative compositions of the resulting chlorinated C_2 hydrocarbon by-products. It is likely that chains in the test process were insufficiently long.

Taking into account these data, we can exclude the possibility of chain termination on the wall in the course of the methane chlorination reaction in a hollow volume, the more so because the surface area to volume ratio (S/V) in an industrial reactor is much smaller than that in a laboratory reactor. De Bernardez and Cassano [11] also made a conclusion that the contribution of termination on the wall is insignificant.

Consequently, it is believed that only cross and quadratic-law (on hydrocarbon radicals) chain termination play the most important role in the bulk thermal chlorination of methane. The cross termination makes a considerable contribution to the course of the process with methylene chloride recycling, when a steady-state concentration of CH_3Cl results from competition between the reactions of its formation upon methane chlorination and consumption in the subsequent chlorination. The fact is that the rate of the process with quadratic-law termination on hydrocarbon radicals depends only on the concentration of chlorine rather than on the concentrations of methane and methyl chloride, whereas it is proportional to the concentrations of methane and methyl chloride to a power of 0.5.

Thus, it seemed reasonable to calculate the rate of methane chlorination on cross and quadratic-law chain termination on hydrocarbon radicals using the published rate constants of elementary steps and then to correct the results with consideration for experimental laboratory, pilot, and industrial-scale data. Thereafter, we intended to derive a single rate equation for the reaction of methane chlorination and to evaluate the contributions of either of these possible components to the overall process.

Table 2 summarizes the Arrhenius equation parameters for the elementary steps of methane chlorination, which were mainly taken from publications concerning more or less comprehensive studies of this process. The parameters used in the calculations are boldfaced.

The numerical values of the constant k_1 were mainly measured by various authors in the region of low pressures, and they belong to a bimolecular reaction (dimensionality of $cm^3\ mol^{-1}\ s^{-1}$). We managed to determine the constant k_1 with the dimensionality of s^{-1} (because of this, the rate constants of chain termination acquired a correct dimensionality of $cm^{1.5}\ mol^{-0.5}\ s^{-1}$) using the rate constant k_{-1} of the reverse reaction measured in the region of high pressures [15] and the equilibrium constant found from thermodynamic data [16].[1]

The rate constants of the chlorination reactions of methane, methyl chloride, methylene chloride, and chloroform at temperatures of 623, 653, 683, 713, 743, and 773 K were calculated from equations corresponding to cross (k_c) and quadratic-law (k_q) chain termination. As applied to the chlorination of methane, methyl chloride, methylene chloride, and chloroform, these equations have the following forms, respectively (constant numbers are specified in Table 2):

$$k_c^{CH_4} = \sqrt{\frac{k_1k_2k_3}{k_{11}}} \quad \text{and} \quad k_q^{CH_4} = k_3\sqrt{\frac{k_1}{k_{15}}};$$

$$k_c^{CH_3Cl} = \sqrt{\frac{k_1k_4k_5}{k_{12}}} \quad \text{and} \quad k_q^{CH_3Cl} = k_5\sqrt{\frac{k_1}{k_{19}}};$$

$$k_c^{CH_2Cl_2} = \sqrt{\frac{k_1k_6k_7}{k_{13}}} \quad \text{and} \quad k_q^{CH_2Cl_2} = k_7\sqrt{\frac{k_1}{k_{22}}};$$

$$k_c^{CHCl_3} = \sqrt{\frac{k_1k_8k_9}{k_{14}}} \quad \text{and} \quad k_q^{CHCl_3} = k_9\sqrt{\frac{k_1}{k_{24}}}.$$

Next, the resulting constants were corrected to obtain the most reliable description of experimental data. Table 3 summarizes the calculated rate constants of methane, methyl chloride, methylene chloride, and chloroform chlorination and the rate constants corrected with consideration for experimental data and converted into the dimensionality of $l^{0.5}\ mol^{-0.5}\ s^{-1}$. From these data, we calculated Arrhenius equation

[1] Data required for the calculation were provided by Yu.A. Kolbanovskii and N.N. Buravtsev (Institute of Petrochemical Synthesis, Russian Academy of Sciences).

Table 2. Arrhenius equation parameters for the elementary steps of the radical chain process of methane chlorination (based on published data)

Step no.	Step	A, $cm^3\ mol^{-1}\ s^{-1}$	$\log A$ [$cm^3\ mol^{-1}\ s^{-1}$]	Activation energy, kcal/mol	References
1	$Cl_2 + M \longrightarrow Cl^{\cdot} + Cl^{\cdot} + M$	2.32×10^{13}	13.37 ± 0.18	46.96 ± 5.72	[12]
		1.1×10^{14}	–	46.99	[13]
		–	15.93	55.9	[14]
		$(5.7 \pm 1) \times 10^{14}$*	–	**56.67**	[15, 16]
2	$Cl^{\cdot} + CH_4 \longrightarrow \dot{C}H_3 + HCl$	$(5.75 \pm 2.78) \times 10^{12}$	–	2.68 ± 0.5	[17]
		$(2.22 \pm 0.97) \times 10^{12}$	–	**2.524 ± 0.126**	[18]
		–	13.7	3.85	[19]
		–	13.5	3.3	[20]
3	$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\cdot}$	–	**12.9**	**2.3**	[19]
		–	13.5	2.42	[21]
		$(2.88 \pm 1.06) \times 10^{12}$	–	0.48 ± 0.2	[22]
		1.07×10^{13}	–	2.15	[23]
4	$Cl + CH_3Cl \longrightarrow \dot{C}H_2Cl + HCl$	–	13.5	3.1	[19]
		$(1.95 \pm 0.40) \times 10^{13}$	–	**2.48 ± 0.5**	[17]
		$(1.08 \pm 0.24) \times 10^{13}$	–	2.2 ± 0.16	[24]
		–	14.2	2.95	[21]
5	$\dot{C}H_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\cdot}$	$(9.12 \pm 1.01) \times 10^{11}$	–	0.98 ± 0.2	[25]
		–	12.0	2.93	[21]
		–	**12.6**	**3.0**	[19]
6	$Cl^{\cdot} + CH_2Cl_2 \longrightarrow \dot{C}HCl_2 + HCl$	$(1.86 \pm 0.69) \times 10^{13}$	–	2.68 ± 1.0	[17]
		–	13.4	3.1	[19]
		–	**13.41 ± 0.07**	**2.96 ± 0.1**	[26]
7	$\dot{C}HCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^{\cdot}$	$(5.13 \pm 2.79) \times 10^{11}$	–	2.46 ± 1.0	[25]
		–	12.0	4.0	[19]
		–	**12.3**	**4.15**	[21]
8	$Cl^{\cdot} + CHCl_3 \longrightarrow \dot{C}Cl_3 + HCl$	$(6.64 \pm 3.0) \times 10^{12}$	–	2.92 ± 0.5	[27]
		–	**12.84 ± 0.04**	**3.32 ± 0.09**	[26]
		–	13.2	3.3	[19]
9	$\dot{C}Cl_3 + Cl_2 \longrightarrow CCl_4 + Cl^{\cdot}$	**$(4.42 \pm 4.0) \times 10^{11}$**	–	**4.73 ± 1.0**	[28]
		–	11.74	5.0	[26]
		–	12.3	6.0	[21]
		–	12.86	5.3	[20]
10	$Cl^{\cdot} + Cl^{\cdot} + M \longrightarrow Cl_2 + M$	–	14.35 ± 0.15**	-1.8 ± 0.44	[14]
		–	15.1**	−1.6	[29]
		$(4 \pm 1) \times 10^{13}$	–	0	[13]
11	$Cl^{\cdot} + \dot{C}H_3 \longrightarrow CH_3Cl$	–	**13.64 ± 0.2**	0	[30]
		–	13.9	0	[21]
		–	14.6	0	[11]
12	$Cl^{\cdot} + \dot{C}H_2Cl \longrightarrow CH_2Cl_2$	–	13.7	0	[21]
		–	**14.4**	0	[11]

Table 2. (Contd.)

Step no.	Step	A, $cm^3\ mol^{-1}\ s^{-1}$	$\log A$ [$cm^3\ mol^{-1}\ s^{-1}$]	Activation energy, kcal/mol	References
13	$Cl^{\cdot} + \dot{C}HCl_2 \longrightarrow CHCl_3$	–	13.7	0	[21]
		–	**14.35**	0	[11]
14	$Cl^{\cdot} + \dot{C}Cl_3 \longrightarrow CCl_4$	–	13.7	0	[21]
		–	**14.4**	0	[11]
15	$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$	–	**13.5**	0	[26]
		–	13.7	0	[30]
16	$\dot{C}H_3 + \dot{C}H_2Cl \longrightarrow C_2H_5Cl$	–	13.1	0	[11]
17	$\dot{C}H_3 + \dot{C}HCl_2 \longrightarrow C_2H_4Cl_2$	–	13.1	0	[11]
18	$\dot{C}H_3 + \dot{C}Cl_3 \longrightarrow C_2H_3Cl_3$	–	13.0	0	[11]
19	$\dot{C}H_2Cl + \dot{C}H_2Cl \longrightarrow C_2H_4Cl_2$	–	12.6	0	[26]
		–	**12.6**	0	[11]
20	$\dot{C}H_2Cl + \dot{C}HCl_2 \longrightarrow C_2H_3Cl_3$	–	12.5	0	[11]
21	$\dot{C}H_2Cl + \dot{C}Cl_3 \longrightarrow C_2H_2Cl_4$	–	12.3	0	[11]
22	$\dot{C}HCl_2 + \dot{C}HCl_2 \longrightarrow C_2H_2Cl_4$	–	12.4	0	[26]
		–	**12.4**	0	[11]
23	$\dot{C}HCl_2 + \dot{C}Cl_3 \longrightarrow C_2HCl_5$	–	12.1	0	[11]
24	$\dot{C}Cl_3 + \dot{C}Cl_3 \longrightarrow C_2Cl_6$	–	11.8	–	[19]
		–	**12.66**	–	[26]
		–	13.9	–	[26]

* A in units of s^{-1}. The value was obtained by multiplying the equilibrium constant of step 1 $K_1 = 10^{1.23}\exp\left(-\frac{56.67}{RT}\right)$ from [15] by the rate constant of the reverse reaction $k_{-1} = (4 \pm 1) \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$ from [16].

** A in units of $cm^6\ mol^{-2}\ s^{-1}$.

parameters for the reactions of methane, methyl chloride, methylene chloride, and chloroform chlorination with cross and quadratic-law chain terminations on hydrocarbon radicals.

We also propose the combined equation

$$w^{RH} = \frac{k_c^{RH}}{\left\{\left(\frac{k_c^{RH}}{k_q^{RH}}\right)^2 \frac{[RH]}{[Cl_2]} + 1\right\}^{0.5}}[RH]^{0.5}[Cl_2].$$

At $\left(\frac{k_c^{RH}}{k_q^{RH}}\right)^2 \frac{[RH]}{[Cl_2]} \ll 1$, it is transformed into the equation $w_c^{RH} = k_c^{RH}[RH]^{0.5}[Cl_2]$, which corresponds to cross termination, whereas it is transformed into the equation $w_q^{RH} = k_q^{RH}[Cl_2]^{1.5}$ with quadratic-law termination at $\left(\frac{k_c^{RH}}{k_q^{RH}}\right)^2 \frac{[RH]}{[Cl_2]} \gg 1$.

The rate equations for the chlorination of methane and chloromethanes (in $mol\ l^{-1}\ s^{-1}$) can be represented in the following form (activation energies in J/mol are specified):

Methane

$$w_c^{CH_4} = k_c^{CH_4}[CH_4]^{0.5}[Cl_2] = 2.31 \times 10^{11}\exp\left(-\frac{129\,000}{RT}\right)[CH_4]^{0.5}[Cl_2];$$

$$w_q^{CH_4} = k_q^{CH_4}[Cl_2]^{1.5} = 1.32 \times 10^{12}\exp\left(-\frac{128\,900}{RT}\right)[Cl_2]^{1.5};$$

Table 3. Calculated and experimental rate constants of the chlorination reactions of methane, methyl chloride, methylene chloride, and chloroform in $l^{0.5}\ mol^{-0.5}\ s^{-1}$

Temperature, K	CH_4		CH_3Cl		CH_2Cl_2		$CHCl_3$	
	calculated	experimental	calculated	experimental	calculated	experimental	calculated	experimental
	Cross termination $R^{\cdot} + Cl^{\cdot} \longrightarrow RCl$ ($w_c = [RH]^{0.5}[Cl_2]$)							
623	5.89	3.38	5.63	5.63	2.51	3.13	0.391	0.598
653	18.4	10.6	17.8	17.8	8.13	10.1	1.30	1.98
683	52.2	29.8	50.9	50.9	23.8	29.6	3.92	5.97
713	137	78.2	133	133	64.5	80.1	10.6	16.2
743	327	188	323	323	160	199	26.7	40.6
773	744	426	733	733	372	462	62.6	95.2
	Quadratic-law termination $R^{\cdot} + R^{\cdot} \longrightarrow R{-}R$ ($w_q = k_q[Cl_2]^{1.5}$)							
623	20.2	20.2	16.4	17.9	4.02	5.80	0.417	0.656
653	63.3	63.3	52.5	57.3	13.5	19.5	1.41	2.22
683	177	177	150	164	40.5	58.5	4.33	6.80
713	458	458	398	435	112	162	12.1	19.0
743	1100	1100	977	1070	281	406	31.1	49.0
773	2490	2490	2210	2410	667	964	74.0	115

$$w_{overall}^{CH_4} = \frac{k_c^{CH_4}}{\left\{\left(\frac{k_c^{CH_4}}{k_q^{CH_4}}\right)^2 \frac{[CH_4]}{[Cl_2]} + 1\right\}^{0.5}}[CH_4]^{0.5}[Cl_2].$$

Methyl Chloride

$$w_c^{CH_3Cl} = k_c^{CH_3Cl}[CH_3Cl]^{0.5}[Cl_2]$$
$$= 5.37 \times 10^{11}\exp\left(-\frac{130900}{RT}\right)[CH_3Cl]^{0.5}[Cl_2];$$
$$w_q^{CH_3Cl} = k_q^{CH_3Cl}[Cl_2]^{1.5}$$
$$= 2.09 \times 10^{12}\exp\left(-\frac{131900}{RT}\right)[Cl_2]^{1.5};$$
$$w_{overall}^{CH_3Cl} = \frac{k_c^{CH_3Cl}}{\left\{\left(\frac{k_c^{CH_3Cl}}{k_q^{CH_3Cl}}\right)^2 \frac{[CH_3Cl]}{[Cl_2]} + 1\right\}^{0.5}}[CH_3Cl]^{0.5}[Cl_2].$$

Methylene Chloride

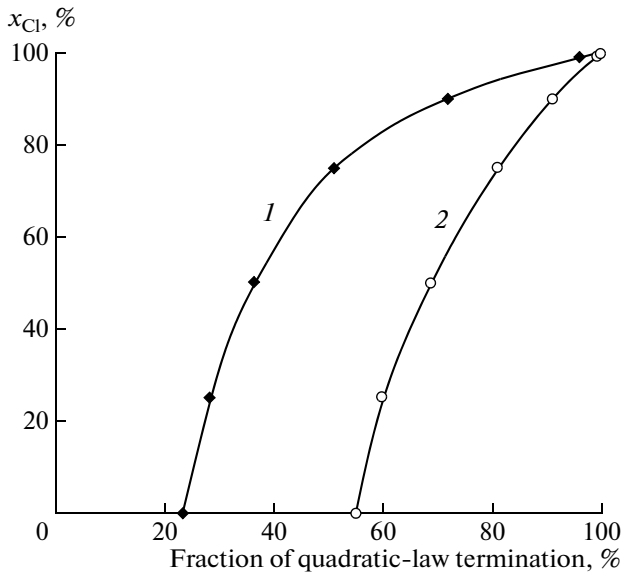
$$w_c^{CH_2Cl_2} = k_c^{CH_2Cl_2}[CH_2Cl_2]^{0.5}[Cl_2]$$
$$= 5.14 \times 10^{11}\exp\left(-\frac{133700}{RT}\right)[CH_2Cl_2]^{0.5}[Cl_2];$$
$$w_q^{CH_2Cl_2} = k_q^{CH_2Cl_2}[Cl_2]^{1.5}$$
$$= 1.57 \times 10^{12}\exp\left(-\frac{136200}{RT}\right)[Cl_2]^{1.5};$$
$$w_{overall}^{CH_2Cl_2} = \frac{k_c^{CH_2Cl_2}}{\left\{\left(\frac{k_c^{CH_2Cl_2}}{k_q^{CH_2Cl_2}}\right)^2 \frac{[CH_2Cl_2]}{[Cl_2]} + 1\right\}^{0.5}}[CH_2Cl_2]^{0.5}[Cl_2].$$

Chloroform

$$w_c^{CHCl_3} = k_c^{CHCl_3}[CHCl_3]^{0.5}[Cl_2]$$
$$= 1.56 \times 10^{11}\exp\left(-\frac{136100}{RT}\right)[CHCl_3]^{0.5}[Cl_2];$$
$$w_q^{CHCl_3} = k_q^{CHCl_3}[Cl_2]^{1.5}$$
$$= 2.94 \times 10^{11}\exp\left(-\frac{138900}{RT}\right)[Cl_2]^{1.5};$$
$$w_{overall}^{CHCl_3} = \frac{k_c^{CHCl_3}}{\left\{\left(\frac{k_c^{CHCl_3}}{k_q^{CHCl_3}}\right)^2 \frac{[CHCl_3]}{[Cl_2]} + 1\right\}^{0.5}}[CHCl_3]^{0.5}[Cl_2].$$

To compare the rates of elementary steps of cross and quadratic-law terminations on hydrocarbon radicals (using the step of methane chlorination as an example), we can consider the corresponding constants of elementary steps specified in Table 2:

$$\frac{w_q}{w_c} = \frac{k_{15}[\dot{C}H_3]^2}{k_{11}[\dot{C}H_3][Cl^{\cdot}]}$$
$$= \frac{3.16 \times 10^{13}[\dot{C}H_3]}{4.37 \times 10^{13}[Cl^{\cdot}]} = 0.723\frac{[\dot{C}H_3]}{[Cl^{\cdot}]}.$$



Contribution of quadratic-law termination on hydrocarbon radicals to the overall rate of chain termination as a function of chlorine conversion: (*1*) industrial-scale reactor and (*2*) pilot reactor.

We find the concentration ratio between the $\dot{C}H_3$ radical and the chlorine atom from the equality of the reaction rates of chain propagation:

$$k_2[Cl^\bullet][CH_4] = k_3[\dot{C}H_3][Cl_2];$$

hence, it follows that

$$\frac{[\dot{C}H_3]}{[Cl^\bullet]} = \frac{k_2[CH_4]}{k_3[Cl_2]}.$$

Finally, we obtain

$$\frac{w_q}{w_c} = 0.723\frac{2.04\times10^{11}[\dot{C}H_3]}{1.23\times10^{12}[Cl^\bullet]} = 0.12\frac{[CH_4]}{[Cl_2]}.$$

The figure shows the contribution of quadratic-law termination on hydrocarbon radicals to the overall rate of chain termination at various chlorine conversions. In an industrial reactor, the concentrations of methane and chlorine in the starting mixture are about 50 and 20%, respectively. Then, at the initial point in time, the contribution of quadratic-law termination to the overall rate of chain termination is ~23%, whereas it is as high as 99.7% at the reactor outlet at a chlorine conversion of 99.9%.

In the pilot reactor, the concentration of chlorine at the inlet of the ring space decreases by a factor of 4 at an injection coefficient of 3 because chlorine does not participate in an intrareactor cycle. Correspondingly, the fraction of quadratic-law termination increases (curve *2*).

From the figure and the results of calculations, we can make a practical conclusion: it is likely that the formation of chlorinated C_2 hydrocarbon impurities as a result of recombination of hydrocarbon and chlorohydrocarbon radicals in the bulk thermal chlorination of methane cannot be avoided.

Thus, in this work, we found rate equations for the reactions of methane, methyl chloride, methylene chloride, and chloroform chlorination using a calculation technique with consideration for experimental data; these reactions occur with cross and quadratic-law chain termination. We also proposed combined equations that imply simultaneous cross and quadratic-law chain terminations. The overall kinetic order of these equations with respect to reactants is 1.5, whereas it should be 2 in accordance with published data. This especially strongly affects the sizes of reactors for methane chlorination at a pressure of 10 atm, the design of which was the subject matter of our studies.

REFERENCES

1. Pease, R.N. and Walz, G.F., *J. Am. Chem. Soc.*, 1931, vol. 53, no. 10, p. 3728.
2. Aglulin, A.G., Bakshi, Yu.M., and Gel'bshtein, A.I., *Kinet. Katal.*, 1983, vol. 24, p. 519.
3. Arai, T., Yoshida, M., and Shinoda, K., *Kogyo Kagaku Zasshi*, 1958, vol. 61, p. 1231.
4. Rozanov, V.N., *Khim. Prom–st.*, 1996, no. 6, pp. 22, 24.
5. Krentsel', B.A., *Khlorirovanie parafinovykh uglevodorodov* (Paraffin Chlorination), Moscow: Nauka, 1964, p. 17.
6. Treger, Yu.A., Kartashov, L.M., and Krishtal', N.F., *Osnovnye khlororganicheskie rastvoriteli* (Most Common Organochlorine Solvents), Moscow: Khimiya, 1984, p. 34.
7. Emanuel, N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1969.
8. Semenov, N.N., *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (Topics in Chemical Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958, p. 227.
9. Gvozd, E.V., Gorozhankina, T.V., and Rozanov, V.N., *Khlornaya Prom–st.*, 1982, no. 4, p. 3.
10. Kalinin, M.V., Gvozd, E.V., Rozanov, V.N., and Treger, Yu.A., in *Rol' kataliza, initsiirovaniya, khimicheskikh dobavok i vliyaniya sredy na protsessy polucheniya khlororganicheskikh produktov* (Roles of Catalysis, Initiation, Chemical Admixtures, and Medium in the Synthesis of Chlorinated Organic Compounds), Moscow: NIITEKhIM, 1991, p. 68.
11. De Bernardez, E.R. and Cassano, A.E., *Ind. Eng. Chem. Process Des. Dev*, 1986, vol. 25, p. 603.
12. Baulch, D.L., Duxbury, J., and Grant, S.J., Montague. D.C, *J. Phys. Chem. Ref. Data*, 1981, vol. 10, suppl. 1, pp. 1-122, 1-129.
13. Borisov, A.A., Kogarko, S.M., and Skachkov, G.A., *Fiz. Goreniya Vzryva*, 1965, no. 1, p. 15.
14. Huybrechts, G., Narmon, M., and van Mele, B., *Int. J. Chem. Kinet.*, 1996, vol. 28, p. 27.

15. Chase, M.W. Jr., *J. Phys. Chem. Ref. Data Monogr.*, 1998, pp. 1–1951.
16. Hippler, H. and Troe, J., *Int. J. Chem. Kinet.*, 1976, vol. 8, p. 501.
17. Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J., and Troe, J., *J. Phys. Chem. Ref. Data*, 1997, vol. 26, p. 521.
18. Seeley, J.V., Jayne, J.T., and Molina, M.J., *J. Phys. Chem.*, 1996, vol. 100, p. 4019.
19. Chiltz, G., Goldfinger, P., Huybrechts, G., Martens, G., and Verbeke, G., *Chem. Rev.*, 1963, vol. 63, p. 355.
20. Bell, T.N., Perkins, K.A., and Perkins, P.G., *J. Phys. Chem.*, 1977, vol. 81, p. 2613.
21. Cabrera, M.I., Alfano, O.M., and Cassano, A.E., *Chem. Eng. Sci.*, 1990, vol. 45, p. 2443.
22. Timonen, R., *Ann. Acad. Sci. Fenn., Ser. A2*, 1988, vol. 218, p. 5.
23. Timonen, R., Kalliorinne, K., and Koskikallio, J., *Acta Chem. Scand., Ser. A*, 1986, vol. 40, p. 459.
24. Tschuikow-Roux, E., Faraji, F., Paddison, S., Niedzielski, J., and Miyokawa, K., *J. Phys. Chem.*, 1988, vol. 92, p. 1488.
25. Seetula, J.A., Gutman, D., Lightfoot, P.D., Rayes, M.T., and Senkan, S.M., *J. Phys. Chem.*, 1991, vol. 95, p. 1068.
26. Kondrat'ev, V.N., *Konstanty skorosti gazofaznykh reaktsii* (Rate Constants of Gas-Phase Reactions), Moscow: Nauka, 1971.
27. Xiao, J.-F., Li, Z.-S., Ding, Y.-H., Liu, J.-Y., Huang, X.-R., and Sun, C.C., *J. Phys. Chem. A*, 2002, vol. 106, p. 320.
28. Timonen, R.S., Russell, J.J., and Gutman, D., *Int. J. Chem. Kinet.,* 1986, vol. 18, p. 1193.
29. Parker, J.K., Payne, W.A., Cody, R.J., Nesbitt, F.L., Stief, L.J., Klippenstein, S.J., and Harding, L.B., *J. Phys. Chem. A*, 2007, vol. 111, p. 1015.
30. Cardelino, B.H., Moore, C.E., Cardelino, C.A., McCall, S.D., Frazier, D.O., and Bachmann, K.J., *J. Phys. Chem. A*, 2003, vol. 107, p. 3708.